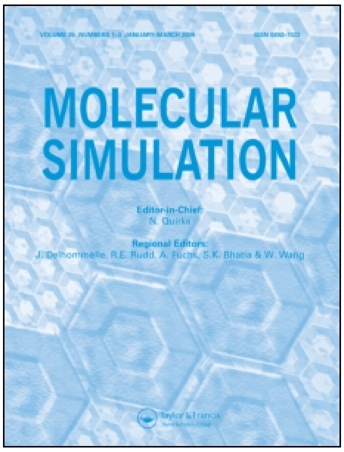

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Growth of Amorphous Silicon: Low Energy Molecular Dynamics Simulation of Atomic Bombardment

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Non-crystalline silicon networks were constructed by atomic deposition and by rapid quenching. The tight-binding molecular dynamics (TBMD) method which had been developed for studying the growth of amorphous carbon structures (Kohary, K., Kugler, S. (2001) "Growth of amorphous carbon: low-energy molecular dynamics (MD) simulation of atomic bombardment," *Phys. Rev. B* 63 193404), was applied. During the relaxations the temperature versus time functions display stretched exponential forms. The most important structural properties were analyzed. The final networks contain significant numbers of triangles and squares.

Keywords: Growth; Amorphous silicon; Tight-binding molecular dynamics simulation; Radial distribution function

INTRODUCTION

Amorphous silicon (a-Si) has been the subject of numerous experimental and theoretical works in recent decades [1]. Neutron diffraction measurements [2–4] and other methods [5,6] were employed on a-Si samples in order to retrieve information about the atomic arrangement, i.e. the radial distribution function (RDF), which contains integrated information about the structures. The results of these experiments suggest that the covalently bonded a-Si are not completely disordered. The bonds between atoms and the coordination numbers are similar to the crystalline phase. First and second neighbor peaks are broadened, but the positions are the same as in the crystalline structure, while the third peak disappears in the measured RDF. The absence of the third peak confirms that there is no characteristic dihedral angle.

In 1985, a continuous random network model of a-Si (WWW model) was constructed by Wooten *et al.* [7] who carried out Monte Carlo (MC) simulations using the classical empirical Keating potential. This defect-free network includes five-fold and sevenfold rings in addition to the six-fold rings of the diamond-like structure. Since then, several computer generated models have been constructed using classical empirical potentials [8–10] or by applying different quantum mechanical methods [11–16], but still the WWW model is considered to be the best three-dimensional atomic scale representation of a-Si. Dangling bonds or even floating bonds (if they exist) are believed to be very rare in this condensed phase of silicon and are not included in the WWW model. Recently, an accurate X-ray diffraction measurement [17] was published in the wide Q range of $0.03–55\,\text{Å}^{-1}$. The most important conclusion of this measurement is that the coordination number is less than four in an implanted a-Si sample, which is controversial with the WWW model of a-Si.

An alternative to MC simulations is molecular dynamics (MD). On the basis of the Car–Parrinello density functional theory (DFT), MD structural simulation was carried out for a-Si having 54 atoms [11]. Larger systems are needed for investigating complex dynamics processes, such as, for example those involved in growth. A frequently applied method is to find a convenient tight-binding (TB) model, which could be employed on more than hundred atoms and could be less time consuming than DFT.

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SIMULATION DETAILS

Rapid cooling of the liquid phase is frequently applied to construct amorphous and glassy structures [8,10–13]. The system is cooled down to room temperature by a rate of 10^{11} to 10^{16} K/s. Another possible approach for constructing an amorphous structure is motivated by the fact that a-Si is usually grown by different vapor deposition techniques in laboratories. We have developed a MD computer code to simulate the real preparation procedure of an amorphous structure, which is grown by atom-by-atom deposition on a substrate. In our recent work [18,19], the growth of amorphous carbon films were simulated by this method. A brief summary is given in the appendix together with the other growth methods used in this paper. All together nine different structures were grown:

(i) Six structures were constructed by method I (see appendix) with 25 ps injection time, and with an average kinetic energy $E_{\mathrm{beam}} = 1$ and 5 eV, at $T_{\mathrm{sub}} = 100$ K substrate temperature (e1T100R5, e5T100R5, e1T100R10, e5T100R10, e1T100R20, and e5T100R20). R5, R10, and R20 indicate different relaxation times (5, 10, and 20 ps, respectively) for both structures after 25 ps injection.
(ii) Three networks (e1T300, e5T300, e10T300) were constructed by method II at $T_{\mathrm{sub}} = 300$ K substrate temperature using our model for faster energy dissipation. Average kinetic energies of bombarding atoms were $E_{\mathrm{beam}} = 1, 5,$ and 10 eV, respectively. The simulation time was 5 ps for these three models. Due to the preparation method the temperature of the films remained 300 K, therefore no relaxation was applied after deposition.

Furthermore, in order to retrieve information on the difference between rapid cooling [10–12] and atom-by-atom deposition on a substrate (melt-quenching and vapor-quenching), we prepared an additional, tenth model (e1T100Q; Q is for quenching) by method III using the atomic structure of e1T100R20 as the initial configuration. This technique can be considered as the computer simulation of splat cooling, where small droplets of melt are brought into contact with the chill-block.

TIME DEVELOPMENT OF RELAXATIONS

After the growth process, when there was no more injected bombarding atom over the networks, the films relaxed with full dynamics for 20 ps. Anomalous behaviors have been observed during relaxations. Temperature versus time functions of these non-equilibrium processes show stretched-exponential forms, $T_{\mathrm{film}}(t) = c + \exp(at^{\beta} + b)$ K. In the case of the e1T100R20 model we obtained the following fitting parameters; $\beta = 0.88$, $a = -0.49\,\mathrm{fs}^{-\beta}$ (t is measured in fs), $b = 7.54$, and $c = 100$ K (substrate temperature) as shown in Fig. 1. For the e1T100Q model, the fitting parameters are similar: $a = -0.46\,\mathrm{fs}^{-\beta}$ and $b = 7.57$. In this latter case the parameter β is equal to 0.95 (<1), also producing a stretched exponential decay. The deposited networks, which have a temperature gradient in the z-direction released a considerable amount of heat. This is attributed to the influence of the substrate kept at a constant temperature. Inside the model e1T100Q (melt-quenching), there is no temperature gradient at the beginning of cooling causing different β parameter. We note here that the search for the best fit is not a well-defined problem in our case. A slight modification in the parameter list can give almost the same quality of the fit. For example, for the e5T100R20 model, $\beta = 1.0$ also displays quite a good fit with $a = -0.41\,\mathrm{fs}^{-1}$, $b = 7.79$ parameters, which represents a normal Debye relaxation.

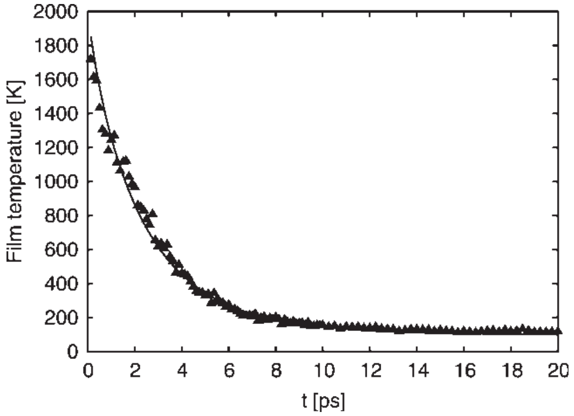

FIGURE 1 The observed stretched exponential function for temperature relaxation in the e1T100R20 film. The best fit was obtained according to $T_{\mathrm{film}}(t) = c + \exp(at^{\beta} + b)$ K. Fitting parameters are $\beta = 0.88$, $a = -0.49\,\mathrm{fs}^{-\beta}$, $b = 7.54$, and $c = 100$ K. The parameter β is smaller than one ($\beta \leq 1$), producing stretched exponential relaxation.

STRUCTURAL PROPERTIES

Density

The structures of different models consist almost of the same number of atoms (between 162 and 177), with a thickness of about 13 Å. In order to ignore the effect of the rough surface on the top of the grown film we identified two different cells: bulk and total sample [18,19]. The top side of the bulk was by 3 Å below the atom having the largest z coordinate. Table I contains the bulk densities of different models. For realistic density calculations one should consider these bulk densities. At $T_{\mathrm{sub}} = 100$ K bulk densities are between 2.3 and 2.5 g/cm^3, while in the quick

TABLE I The table below contains the number of silicon atoms (*Nr.*) in the bulk of the films, in addition to the percentage of atoms with different coordination numbers (Z), the average coordination number $\langle Z \rangle$, the thickness h (in Å) and the density ρ (in g/cm^3). The first neighbor shell was equal to 2.6 Å

Model	*Nr.*	$Z = 2$	$Z = 3$	$Z = 4$	$Z = 5$	$Z = 6$	$\langle Z \rangle$	h	ρ
e1T100R5	140	7.1	10.7	70.0	7.1	0.0	3.7	10.1	2.5
e1T100R10	134	3.0	14.9	67.9	12.7	0.7	3.9	9.8	2.4
e1T100R20	134	3.0	12.7	71.6	10.4	1.5	3.9	9.8	2.4
e5T100R5	151	7.9	23.8	51.7	10.6	0.0	3.5	10.6	2.3
e5T100R10	152	5.9	23.0	50.0	20.4	0.7	3.9	10.7	2.3
e5T100R20	152	4.6	18.4	51.3	23.0	2.0	4.0	10.7	2.3
e1T300	151	7.9	16.6	53.6	15.2	2.6	3.8	10.8	2.4
e5T300	135	6.7	19.3	47.4	20.0	3.0	3.9	9.4	2.8
e10T300	142	7.0	19.7	52.1	19.7	0.7	3.9	9.7	2.7
e1T100Q	122	1.6	13.9	74.6	8.2	0.0	3.9	9.1	2.4

energy dissipation models ($T_{\mathrm{sub}} = 300\,\mathrm{K}$) the structures possess higher densities (2.4–2.8 g/cm^3). For crystalline silicon the density is equal to 2.33 g/cm^3, which is lower than the values we obtained for a-Si, i.e. our tight-binding molecular dynamics (TBMD) simulation provided more dense structures. The void-free WWW network [7] has a similar result. There was no significant change in the densities during the relaxations.

Radial Distribution and Bond Angle Distribution Functions

In Fig. 2, the first and the second main peaks of the RDF are shown in the e1T100Q model. All the other models provide similar RDFs. Contrary to our simulated a-C systems [18,19], the position of the border between the first and the second neighbor shell cannot be clearly defined. Usually, the results of diffraction measurements on amorphous samples have a similar problem because the first two main peaks in RDF obtained by Fourier transformation overlap each other. A possible solution is to consider the largest Si–Si distance which has ever been measured. A systematic analysis of structural data has been carried out using the Cambridge Structural Database [20]. The majority of measured Si–Si distances are less than 2.6 Å. Only 4 out of 3578 bonds (0.1%) are a bit larger than 2.6 Å (see Fig. 1 in Ref. [20]). Taking 2.6 Å for the first neighbor shell, two snapshots of the e1T100R20 and the e1T100Q networks are shown in Fig. 3. The substrates with $T_{\mathrm{sub}} = 100\,\mathrm{K}$ remained similar to the crystal lattice, although a Si atom left the substrate and a bombarding atom replaced this atomic site in both cases.

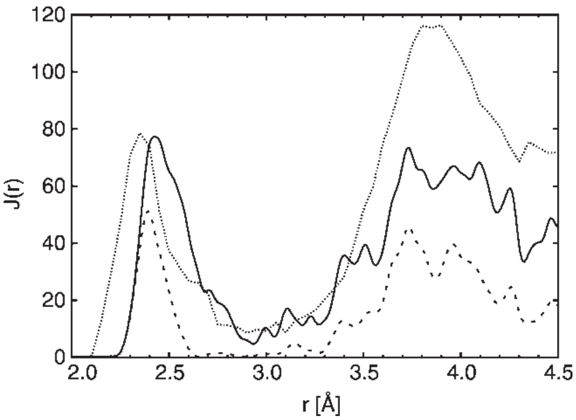

FIGURE 2 The first and the second neighbor peaks in the RDF for the e1T100Q model (solid line). The dotted line shows the experimental RDF, reported in Ref. [4]. The first and second neighbor peaks overlap each other. The model potential applied in these simulations overestimates the average first neighbor distance. The dashed line represents the $\mathrm{Si}_{Z=4}$–$\mathrm{Si}_{Z=4}$ partial RDF, which belongs to distances between $Z = 4$ coordinated silicon atoms, taking the first neighbor shell equal to 2.6 Å.

The TB potential applied in our computer experiments slightly overestimates the first neighbor distance as was predicted and reported earlier by the authors of the potential [21]. However, if the potential would provide only silicon atoms with a coordination number equal to four ($Z = 4$), the position of the peak for the first neighbor shell would be at the right place as it can be seen in Fig. 2. The left part of the first main peak is dominated by $\mathrm{Si}_{Z=4}$–$\mathrm{Si}_{Z=4}$ distances (dashed line). The distances between silicon atoms with different coordination numbers than four contribute to the right part (larger bond lengths) of the peak.

The average coordination number in a-Si is approximately four. This value can be provided in our models if we choose 2.6 Å for the first neighbor shell. Taking 2.82 Å as a limit for the first neighbor shell to calculate the statistics of the models, we received coordination numbers close to five, which is between the average coordination number in amorphous ($\langle Z \rangle \approx 4$) and liquid ($\langle Z \rangle \approx 6$) silicon.

The main contribution to the bond angle distribution arises from angles between 80° and 125° (see Fig. 4). There is also a significant contribution from bond angles close to 60°.

Ring Statistics

A surprising result was found in the ring statistics. We defined a ring as a closed path, which starts from

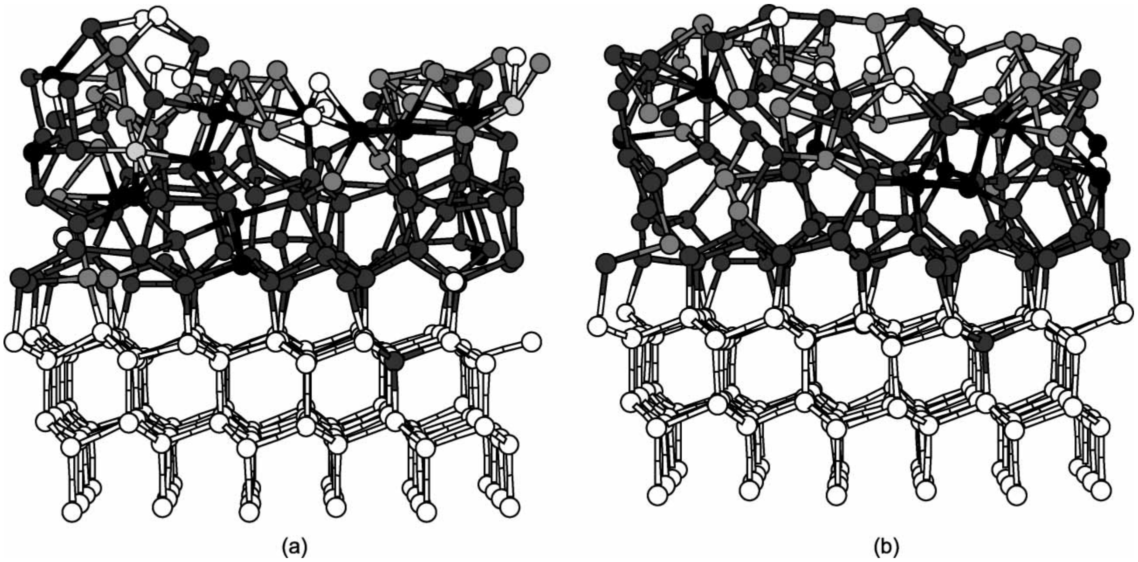

FIGURE 3 Snapshots of the e1T100R20 (left) and the e1T100Q (right) models are shown after growth and relaxation. The substrates (open circles at the bottom) with $T_{\rm sub} = 100\,\rm K$ remained similar to the crystal lattice during the growth. Slate gray, gray and black atoms are threefold, fourfold and fivefold-coordinated, respectively. The remainder of the open circles correspond to two-fold and one-fold coordinated atoms. For a color version see http://www.phy.bme.hu/∼kohary/aSifigures.html.

a given atom walking only on the first neighbor bonds. The size of a ring is the number of atoms in a closed path. The ring statistics are displayed in Table II. The networks prepared by our models have a significant number of squares. Furthermore, triangles are also present in the atomic arrangements. Most of the theoretical models for a-Si do not contain such structural fractions. It seems to be an important result although a neutron diffraction measurement carried out on a pure evaporated a-Si sample, and evaluated by the reverse MC method had a similar conclusion [4]. Nevertheless, the systematic analysis of the structural data of the Cambridge Structural Database suggests that the equilateral triangles and near planar squares can also be natural local configurations inside the atomic arrangements of a-Si [20]. All of these three independent pieces of evidence support the existence of triangles in a-Si structures.

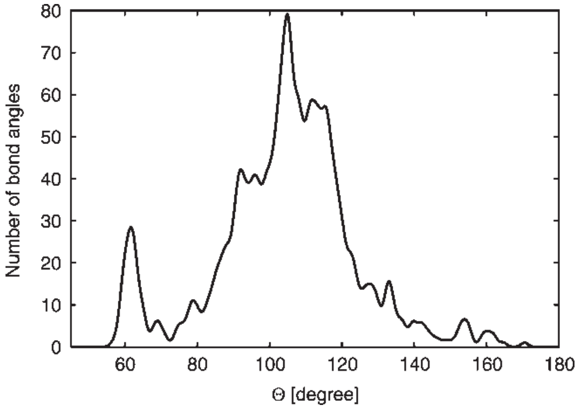

FIGURE 4 The bond angle distribution of the e1T100R20 network is shown after relaxation. There are significant contributions around 60° and 90° due to triangles and squares in the atomic arrangement.

Significant differences can be found in the ring statistics between samples constructed by rapid quenching and by the atom-by-atom deposition methods. From Table II, it can be seen that for the model e1T100Q (rapid quenching) the number of rings is much lower than for e1T100R20, i.e. models prepared by different techniques have different medium range order. Apart from the ring statistics all the other structural parameters of these models were similar.

SUMMARY

The main goal of our work was to simulate a-Si structures. We have developed a TBMD computer code to simulate the preparation procedure of a-Si networks, which are grown by a vapor deposition technique. Nine structures were simulated by this

TABLE II Ring statistics up to seven-member rings taking the first neighbor shell equal to 2.6 Å. (*N* is the size of a ring)

Model	$N = 3$	$N = 4$	$N = 5$	$N = 6$	$N = 7$
e1T100R5	12	10	50	86	95
e1T100R10	25	10	61	85	93
e1T100R20	9	14	68	89	102
e5T100R5	11	9	51	45	65
e5T100R10	14	21	74	84	96
e5T100R20	18	20	78	103	116
e1T300	13	9	33	36	46
e5T300	13	8	44	31	33
e10T300	7	8	16	19	12
e1T100Q	6	13	63	72	86

method. An additional tenth model (e1T100Q) was prepared by rapid cooling in order to make a comparison between the atom-by-atom deposition on a substrate and the melt-quenching preparation techniques.

The most important difference we have found between the models prepared at various conditions, is in the ring statistics, i.e. in the medium range order. In our simulations, triangles and squares are also present in the atomic arrangement. Two other independent pieces of evidence also support the existence of triangles in a-Si structures. Nevertheless, the fragments like equilateral triangles have never been considered at electronic density of states calculations or with unsolved problems such as the breaking of weak bonds by prolonged illumination, which is the major mechanism for the light-induced defect creation [22].

The TB model potential used in our computer experiments slightly overestimates the bond distances, giving values which were observed previously in liquid forms [23]. A more important problem is that the TB potential provides overcoordinated atomic sites (five-, and even six-fold coordinated atoms) during the a-Si simulations. The six-fold coordinated atoms we obtained can be found in the liquid phase of silicon instead of in the amorphous structure. The well-known Stillinger–Weber classical empirical potential for silicon had a similar difficulty, but this has recently been successfully modified [24].

Acknowledgements

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APPENDIX

In our simulations, the transferable tight-binding (TB) Hamiltonian of Kwon *et al.* [21] was applied to describe the interaction between silicon atoms. This group had already developed an excellent TB potential for carbon systems and we successfully applied it for the description of the amorphous carbon growth [18,19]. All the parameters and functions of the interatomic potential for silicon were fitted to the results of the local density functional calculations. The TB potential reproduces the energies of different cluster structures, the elastic constants, the formation energies of vacancies and interstitials in crystalline silicon. According to the authors [21], the only disadvantage of this TB model is that the bond lengths inside small clusters are a bit longer than those derived from other theoretical calculations or from the experiments.

We used three different methods to prepare our amorphous structures:

- **Method I**. A rectangular diamond lattice cell containing 120 silicon atoms was employed to mimic the substrate. There were 16 fixed atoms at the bottom. The remaining atoms could move with full dynamics. The simulation cell was open along the (111) direction (positive z-axis) and periodic boundary conditions were applied in x, y directions. The kinetic energy of the atoms in the substrate were rescaled at every MD step ($\Delta t = 0.5\,\mathrm{fs}$) in order to keep the substrate at a constant temperature. In the deposition process the frequency of the atomic injection was $1/125\,\mathrm{fs}^{-1}$ on average. This flux is orders of magnitude larger than the deposition rate commonly applied in experiments. However, the low substrate temperature (100 K) during simulations cause faster energy dissipation and this may compensate the high deposition rate. The initial kinetic energies of the bombarding atoms in this case were dissipated by the interaction with the surface atoms. In our first set of simulations there was no *ad hoc* model of energy dissipation.
- **Method II**. To reduce the central processing unit (CPU) time of this time-consuming computer simulation, we have developed a different method. The velocities of bombarding atoms were modified by the following procedure. When a bombarding silicon atom arrived closer to any substrate atom than a "critical distance", it became a member of the substrate atomic set, i.e. their total kinetic energy was also rescaled in every MD step to a given substrate temperature. The chosen critical distance was 15% larger than the bond length in crystalline silicon (2.36 Å). This is a simple model to speed up the energy dissipation and a plausible interpretation of the inelastic collision phenomena.
- **Method III**. To prepare a reference model similar to those structures made by the liquid quench method we used the following method. The temperature of the film of one of our final structures was increased up to 3500 K as an initial state (liquid phase) while the substrate temperature remained the same. After this melting, the trajectories of the silicon atoms were followed by full dynamics within 7.5 ps. The substrate temperature kept at 100 K leads to the cooling of the film above the substrate.

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